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The effects of assimilation on sulfide saturation and the formation of norite-hosted Cu-Ni deposits in the Duluth Complex, Minnesota

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In this contribution, we use thermodynamically constrained geochemical models to study how black shale assimilation affected sulfide saturation and norite-hosted Cu-Ni deposit formation in the Duluth Complex (DC), Minnesota. These models show in unprecedented detail how progressive assimilation changes the chemical composition of the magma leading to earlier and increased sulfide saturation compared to pure fractional crystallization. The models indicate that at least half of the S in the wall-rock black shale must partition to the assimilated partial melt to form the norite-hosted Cu-Ni deposits. Against the general consensus, sulfide saturation seems to occur at temperatures too low for FeS sulfide melt formation, which explains the dominantly low-grade disseminated sulfide deposits in the DC.

Keywords: Sulfide saturation, Duluth Complex, Cu-Ni deposit, Magma Chamber Simulator

1. Introduction

Sulfide saturation is a process which occurs when the sulfur (S) content in a melt exceeds the amount that can be dissolved, and as a result, a liquid or solid sulfide phase forms. In addition to the absolute S content of the melt, composition and temperature (T) of the silicate melt affect the timing and degree of sulfide saturation (Smythe et al. 2017), and hence control the formation and grade of base metal (e.g., Cu and Ni) sulfide deposits.

In continental settings, mantle-derived magmas are typically sulfide undersaturated at the time of intrusion or extrusion. As these magmas cool and crystallize, they eventually reach sulfide saturation, and sulfides start to form in cotectic proportions. Such cotectic proportions are rarely high enough to form economical sulfide deposits. Accordingly, with few exceptions, all the economically important magmatic Cu-Ni deposits worldwide formed as magmas assimilated wall-rocks (Leshar, 2019).

Assimilation of S-bearing wall-rocks can directly increase the S content of the melt, but sulfide saturation can be further intensified by changes in the major element composition of the assimilating melt. Until recently, only the compositional effects of assimilating bulk wall-rocks or putative partial melts could be tested by simplified chemical mixing models. Consequently, the detailed effects of assimilation on sulfide saturation are largely unknown.

The Magma Chamber Simulator (MCS) is a thermodynamically constrained modelling tool designed especially for fractionally crystallizing (FC) magmas experiencing open system processes such as assimilation and/or magmatic recharge (Bohrson et al. 2014, Bohrson et al. 2020). Heat and mass balance between the magma, wall-rock, and possible recharge magmas are accounted for and phase equilibria are modelled accordingly. This provides a sophisticated approach for assimilation, where its continuous effect on compositional evolution of the magma can be monitored. Both major and trace elements (and isotopes) can be tracked within the different reservoirs in the model (Bohrson et al. 2020, Heinonen et al. 2020). Hence, the MCS

can provide new detailed insight into how assimilation-fractional crystallization (AFC) lead to formation of sulfide deposits.

We studied the differences in the silicate melt's ability to dissolve S during FC and AFC using the MCS and the sulfide saturation model of Smythe et al. (2017). Due to the lack of thermodynamic data on sulfides, S was modelled with the MCS trace element protocol (Heinonen et al. 2020). These models show in detail how assimilation of a progressively melting wall-rock effectively reduces the amount of S required for sulfide saturation. This together with excess S assimilated from the wall-rock leads to early sulfide saturation and an increased amount of sulfide precipitation in the magma.

2. Geological settings

The Duluth Complex (DC), Minnesota, is a 1.1 Ga composite mafic layered intrusion hosting some of the largest known Cu-Ni deposits in the world (Miller et al. 2002, Figure 1). All of the deposits are situated at the proximity of the footwall contact of the intrusions (Figure 1). Troctolitic cumulates host some 70% of the deposits consisting mostly of disseminated sulfides. The remaining 30% of the deposits consist of semi-massive to disseminated sulfides and are hosted by noritic rocks as well as footwall rocks and xenoliths. Based on S isotopes, it has been estimated that approximately 75% of the S in some of the deposits derived from the adjacent Paleoproterozoic Virginia Formation (VF) black shale, which contains 6000 ppm S on average (Ripley 1981, Rao and Ripley 1983, Figure 1).

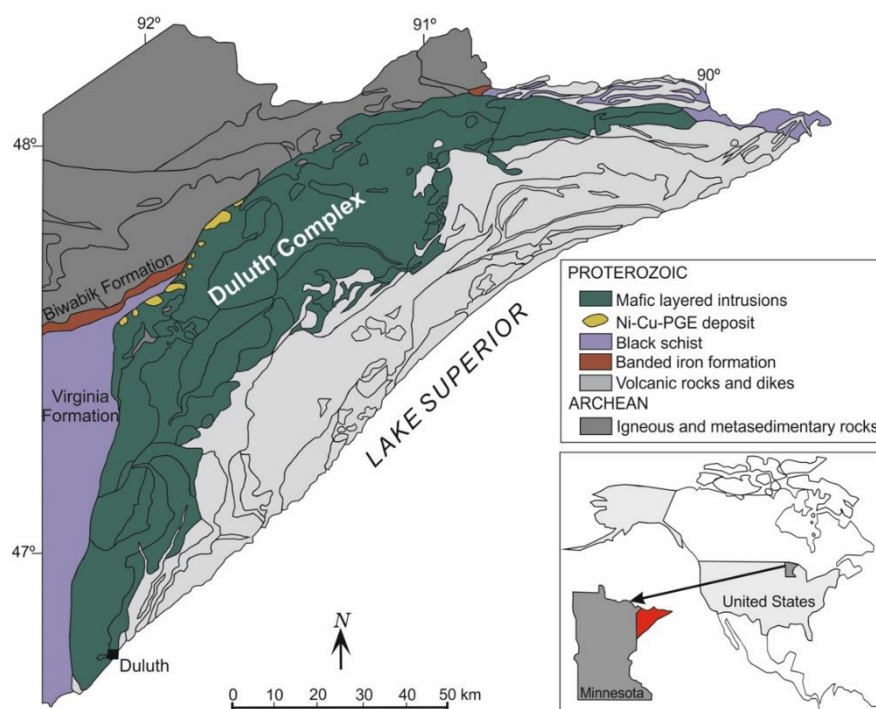


Figure 1. The geological map showing the Duluth Complex and the adjacent rocks.

3. The MCS and sulfide saturation model results

In the MCS models, we used composition of a cogenetic basalt from the North Shore Volcanic Group (Figure 1) as the parental magma for the DC intrusions. We set the initial oxygen fugacity to $\Delta\text{FMQ} -2$ and tested different H_2O contents (dry to $2.25 \text{ H}_2\text{O}$) for the parental magma. The

modelled cumulate stratigraphies show that the amount of troctolitic cumulates (*sensu lato*) positively correlates with the H₂O content of the magma (Figure 2). Comparison with the natural cumulate from a DC intrusion (Severson et al. 1996) reveals that the magma must have been hydrous (≥ 1 wt.% H₂O) to produce the dominantly troctolitic cumulates (Figure 2).

The parental melt with 1 wt.% H₂O was used for the AFC models. The VF black shale (Figure 1) wall-rock was preheated to 600 °C and the initial wall-rock magma mass ratio was 0.5. In this model, norites replace troctolites after assimilation of ~20 wt.% (relative to parental melt) of wall-rock partial melts (Figure 2). The magma assimilates 38 wt.% of wall-rock partial melts in total until the T of the magma is too low for further assimilation. The subsequent FC produces first noritic (*sensu lato*) cumulates before the formation of anorthositic troctolite (Figure 2).

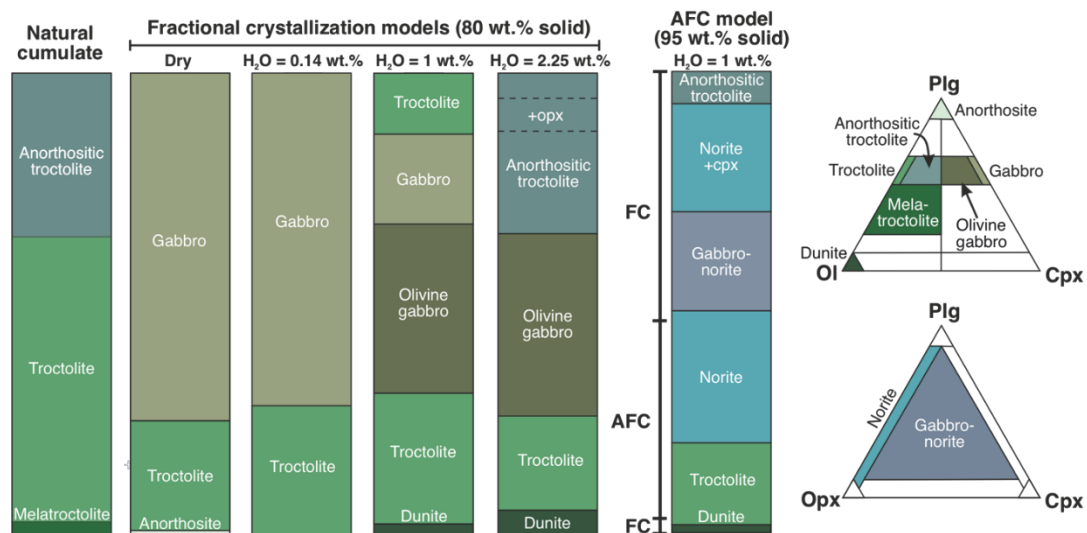


Figure 2. Natural cumulate stratigraphy (Severson et al. 1996) from the Duluth Complex compared with the cumulate stratigraphies produced after 80 wt.% of fractional crystallization (FC) in the models with different initial parental melt H₂O contents. The cumulate sequence (95 wt.% relative to the parental melt) formed in the assimilation fractional crystallization (AFC) model for the parental melt with 1 wt.% H₂O is shown on the right.

Sulfide saturation models for the parental melt with 1 wt.% H₂O and 800 ppm S experiencing FC and AFC are compared to show the effect of assimilation on S content at sulfide saturation (SCSS) in the magma. The initial S content in the wall-rock is 6000 ppm. The FC model reaches SCSS when ~27 wt.% of the melt has crystallized and T is ~1145 °C. When assimilation begins in the AFC model, the SCSS decreases rapidly relative to FC due to decreasing FeO and increasing H₂O content in the magma (Figure 3). In the model, where S is compatible ($D^S = 100$) to the residual wall-rock, the magma reaches SCSS at ~13 wt.% solids and T of ~1140 °C (Figure 3). When S is equally compatible to wall-rock residual and assimilated partial melt, the SCSS of the magma is reached at ~8 wt.% solids and T of ~1150 °C (Figure 3). If S is completely incompatible to the residual wall-rock ($D^S = 0.001$), the magma reaches SCSS when ~5 wt.% of the system has solidified and the T is ~1150 °C (Figure 3). In all cases, the T at SCSS is lower than the solidus of an FeS sulfide melt (~1190 °C). The maximum proportion of black-shale derived S in the magma is ~6 wt.% with $D^S = 100$, ~74 wt.% with $D^S = 1$, and 78 wt.% with $D^S = 0.001$.

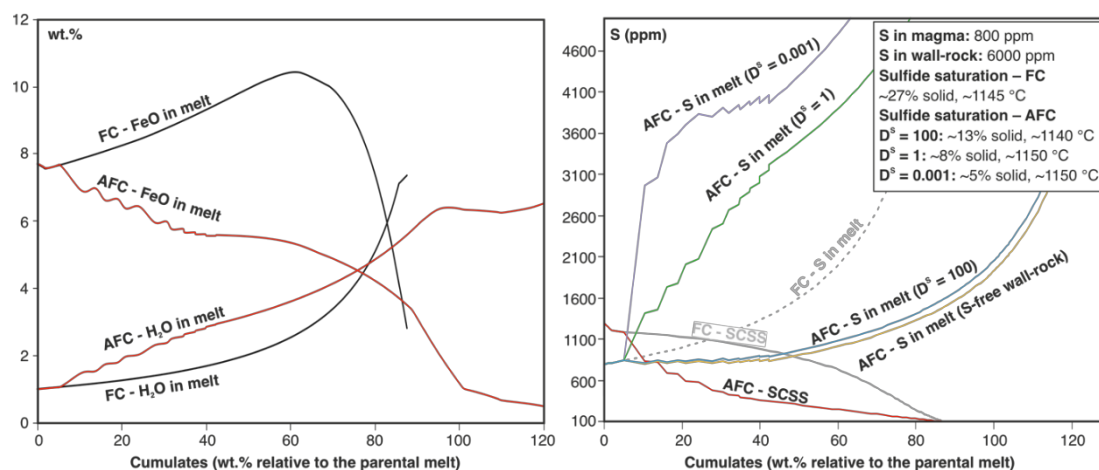


Figure 3. On the left, fractional crystallization (FC) and assimilation fractional crystallization (AFC) models for FeO and H₂O contents of the Duluth Complex parental magmas with 1 wt.% H₂O. On the right, S content at sulfide saturation (SCSS) are shown for the same models. The partition coefficients for S (D^S) are relative to wall-rock residual.

4. Conclusions

Our models show that the troctolitic cumulates of the DC likely formed by FC of a hydrous magma, whereas the formation of the noritic rocks requires >20 wt.% assimilation of partial melts from the VF black shale. To meet the isotopic criteria of ~75 wt.% black-shale derived S in the norite-hosted DC Cu-Ni deposits, at least half (wall-rock $D^S \leq 1$) of the VF S must partition to the assimilated partial melt. In all the models, SCSS is reached at T lower than FeS solidus indicating that only minor Cu-rich residual sulfide melt could have formed in the DC magmas. Coalescence of solid sulphides is ineffective, which is compatible with the dominantly low-grade Cu-Ni deposits.

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